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Determination of the Relative Velocities
# of The
Ions of Silver Nitrate
in
Mixtures of the Alcohols and Water
and on the
Conductivity of Such Mixtures.

By

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DISSERTATION

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Historical Review.

The early investigators noticed that when an electric current was passed through an electrolyte changes in concentration were produced.

This phenomenon was made manifest in his brilliant experiments by Davy(1), but the first attempted explanation was given by Berzelius and Hisinger(2).

No further progress was made in solving this problem until the time of Faraday(3), who noticed that if a current is passed through a solution of copper sulphate, using copper poles, the solution around the cathode becomes lighter blue, while around the anode it becomes darker blue. This same phenomenon was observed by Gmelin(4) two years later. Pouillet(5) observed a similar phenomenon in a gold solution.

Ten years later Smee(6) still advocated the theory put forward by Faraday and published many experiments to prove this theory. He came to the conclusion that when a solution of a metallic salt was subjected to the influence of a cur-

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(1). Gilbert Ann. Bd. 28, 26; Phil. Trans. 1807, 28.
(2). Ann. d. Chemie vol. 1, 174.
(3). Pogg. Ann. 32, 436, (1834).
(4). Pogg. Ann. [illegible], 5, (1836).
(5). Comp. Rend. 20, 1544, (1845).
(6). Phil. Mag. [illegible], [illegible], (1840).

rent that water was decomposed and the oxygen and hydrogen passed in different directions, and the hydrogen at the instant of decomposition on the negative pole acted upon the copper sulphate and other metallic salts in the same manner as iron or zinc would in the same solutions.

Daniell and Miller (1) working jointly put forward the conception of the interchange of ions. From the results of their investigation they came to the conclusion that the usual conception was wrong. They devised an apparatus which was divided into three cells by two porous walls. In this they electrolysed copper and zinc sulphates. They proved in this investigation that the two ions of each of these two salts evidently traveled with different velocities, but they could not interpret their results. They also worked on other metallic salts, but the conclusion that they drew from the results found in the copper and zinc solutions did not hold in the other cases.

The subject was left here until Hittorf (2) undertook his elaborate series of experiments and showed that these changes in concentration were caused by a difference in the velocities of the anion and cation (in copper sulphate the anion SO traveling faster than the cation Cu).

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(1). Phil. Trans. I, (1844); Pogg. Ann. 64, 18, (1845).
(2). Pogg. Ann. 89, 177 (1853); 98, 1 (1856); 103, 1 (1858); 106, 337, 513, (1859).

Hittorf in his investigation went back to the explanation put forward by Grotthus. He showed that by analysis of the solution around the electrodes, the ratio between the velocities of the two ions could be calculated.

In his work he devised several forms of apparatus depending upon the nature of the salt under investigation. In principle, however, they were very similar, consisting of a vertical tube divided into cells by porous diaphragms, the cathode being inserted in the upper cell and anode in the lower cell.

The form of apparatus used by him has some very objectionable features. The membranes are liable to be reacted on by the electrolyte during the electrolysis, and produce some very serious errors.

Hittorf also determined the ratio between the velocities of the ions of a large number of salts and studied the effect of changing the conditions of the experiment. He first studied the effect of changing the strength of the current. By using currents of several different strengths he was able to show that the relative velocities of the ions was independent of the strength of the current.

The next question to settle was the effect of concentration of the solution on the relative migration velocities. To settle this question he investigated solutions of copper

sulphate ranging between normal and twentieth normal.

He found from these determinations that the migration velocity of the copper ion was with respect to the SO_4 ion increased as the dilution increased until a certain dilution was reached, beyond which it became constant. He also proved in this connection that in some cases the velocity of the cation decreased with increase in dilution of which a notable example is silver nitrate.

The third condition which Hittorf thought might effect the velocity of the ions was the effect of temperature. From his work on such salts as copper sulphate between 4° C and 20° C he concluded that the temperature coefficient was zero.

After the work of Hittorf very little was done in this field until the work of F. Kohlrausch(1), in which he showed that a very important relation exists between the velocities of the ions and the conductivity of solutions.

Kohlrausch came to the three following conclusions. First. If dilute solutions of various salts be prepared having their strengths proportional to the chemical equivalents of the salts, then the specific conductivities of these solutions are all of the same order of magnitude.

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(1). Wied. Ann. 26, 1 and 145, (1879).

Second. In dilute solutions, under a fixed electromotive force, each of the ions moves through the liquid with a fixed velocity, dependent on its own chemical nature, and independent of that of the other ion. This is termed the law of independent migration.

Third. The influence of change in temperature upon conductivity tends, as dilution increases, to a limiting value, the temperature coefficient being the same within narrow limits.

In Kohlrausch's (1) investigation he determined the specific conductivities of solutions of varying strength, from saturation to dilution of a few percent, and from observations thus obtained deduced by extrapolation the conductivity in more dilute solutions.

In his determination of the conductivity of salt solutions he measured the constant (C + A), the sum of the velocities of the anion and cation which approaches a constant value in very dilute solutions, so that he was able to assign to certain ions values for c and a which are known as specific ionic velocities.

Kohlrausch calculated the values for the specific veloci-

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(1). Wied. Ann. 26, 191, (1885).

ties of different ions, from measurements of the conductivities of salt solutions, and their migration constants, on the supposition that all the molecules of the salt present in solution are actively concerned in carrying the current. It is supposed that the ratio of the numbers of the active and the inactive molecules represents in reality the average ratio of time during which each molecule is active to the time during which it is inactive. According to this every molecule is in turn active, but at any instant only a certain portion of molecules are active. This is of course equivalent to supposing a certain fixed fraction of the whole number of molecules to be active as far as such phenomena as osmotic pressure are concerned, but when the velocity of the ions is concerned it is quite different.

Kohlrausch saw that in any given solution of a salt, the average velocity is dependent on the driving force or fall of potential on the specific velocities and the coefficient of ionisation or $(C + A) = \pi\lambda(c + a)$, where $C + A$ are the average velocities and $c + a$ the specific velocities. He found, comparing the conductivity of solutions of definite dilution, that two electrolytes having a common anion and different cations, have the same difference in conductivity as the electrolytes having another anion and the same cations as the

first two electrolytes. The same results were obtained when salts were compared having a common cation. In each case the differences are practically the same within the limits of experimental error. Then, from the above relation the conductivity of a solution at infinite dilution is the sum of two constants, one depending on the anion and the other on the cation.

Since the conductivity of a solution at infinite dilution, deals with comparable numbers of ions, this value must depend upon the velocity with which they move, thus this constant is then proportional to the velocity of the cation and anion.

Now if we represent by c the velocity of the cation, and by a the velocity of the anion

$$\mu_\infty = c + a$$

If expressed in words, the velocity with which any ion travels is a constant for a given solvent and a given potential gradient, and is independent of the nature of the other ion or ions with which it is present in the solution.

This law, as is readily seen, only holds for very dilute solutions as it is only in very dilute solutions that the value of μ_∞ can be obtained directly by experiment.

Ostwald[1], however, has shown that the law of Kohlrausch is of more general application and can be used with concentrated as well as with dilute solutions.

If the solutions are concentrated they will not necessarily be completely dissociated, and, therefore the amount of dissociation must be taken into account. The law of Kohlrausch then becomes

$$\mu_v = \alpha (c + a)$$

α representing the amount of dissociation.

In these investigations by Kohlrausch and Ostwald they have demonstrated that the molecular conductivity of an electrolyte increases with the dilution, and reaches at a definite limit a maximum value, and that this value as shown above is the sum of the two independent constants which are in fact the velocities of the ions at infinite dilution in terms of the conductivity units. It is, then, obvious that the law of Kohlrausch can be used to determine the velocity of ions.

This value μ_∞ can be determined directly by the conductivity method for measuring the molecular conductivity, and we can determine the ratio between these two velocities by Hittorf's method for determining the relative migration numbers, and thus from the two equations

$$\mu_\infty = c + a \qquad (1)$$

$$\frac{c}{a} = \frac{u}{1} \qquad (2)$$

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(1). Zeitr. f. phys. Chem. [illegible], [illegible].

where A & C represent the velocities of the ions at infinite dilution and c/a is the ratio found by Hittorf's method. By this method the velocity of the ions must be the same, whether determined for one substance or for any other substance in which it may occur. This point was tested by Kohlrausch for several ions, and their velocities were calculated for several salts and found to be the same in every case.

Up to this time the numbers given by Kohlrausch for the absolute velocity of different ions have been deduced from theoretical grounds, and the only verification to which they have been subjected was by showing that from them the observed conductivities and migration coefficients of a number of solutions can be calculated.

The first direct measurement of the mean velocity of ions was made by Lodge (1), who observed the progress of a layer which moved through a gelatin solution and thus marked the advance of the ion whose velocity is wished to determine.

The values obtained experimentally by him agreed well with those calculated by Kohlrausch.

The method of Lodge, however, was open to objections,

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(1). Brit. Ass. Report. (1886), 389; (1887), 129.

since the influence of the gelatin was quite unknown the assumption was made that all ions if affected at all would be influenced to the same extent. Further, since the observed velocity is conditioned by the fall of potential, e, it is necessary that the fall should be regular and that it should be known before C can be determined. Lodge did not fulfill these conditions in his experiments. He assumed that in the tube, which was 40 cms. long and with a difference of potential of 40 volts between the ends, the fall in potential was 1 volt per centimeter. In fact the contents of the tube, originally homogeneous, became heterogeneous, by the passage of the current, and thus the fall in potential could not remain regular. That the fall was not very irregular is shown by his values for the hydrogen ion, which compare fairly well with those calculated by Kohlrausch.

Up to this time no form of apparatus had been devised which did not use either a porous diaphragm or a gelatin solution. Loeb and Nernst (1) devised a form of apparatus which did away entirely with the porous diaphragm used by Hittorf. Their apparatus was of the form of a Gay-Lussac burette with the electrode around which the solution became more concentrated placed in the lower portion.

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(1). Ztschr. phys. Chem. 2, 948, (1888).

In their investigation they worked upon eight silver salts, first determining their conductivity and calculated their ionic velocity according to the principle laid down by Kohlrausch with the view of still further testing the modern view of electrolysis.

From their results the values were practically constant and gave satisfactory evidence for the truth of the theory, the number varying only within narrow limits. They also calculated the values for the velocities of the other ions, and studied the effect of temperature on the velocity of the ions and found that rise in temperature slightly diminished the relative velocity of the swifter ion; all ions thus tended to move with the same velocity.

Their method is subject to several sources of error. There is no means of separating the solutions after electrolysisto be removed for analysis, and no means to prevent diffusion. Again, it is better to measure the current by some direct method.

The methods of Kistinkoffsky (1) and also of Bein (2) are quite similar to that of Loeb and Nernst. Both have made slight

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(1). Ztschr. phys. Chem. 6, 97, (1890).
(2). Weid. Ann. 46, 29, (18[illegible]).

modifications in the apparatus, but the same objections which apply to the apparatus of Loeb and Nernst hold in these cases.

Kistinkoffsky used his method to advantage to determine the ions of some complex salts, and in this connection did some very interesting work.

Whetham (1), avoiding the use of a gelatin solution, also all porous diaphragms, measured the velocity of the moving boundary between two aqueous solutions. In this method he used two salts that had a common ion.

A bounding layer between the salt solutions was observed, and absolute instead of relative measurements made. Any uncertainty as to the regularity of the fall of potential was avoided by the selection of such pairs of solutions which had equal or nearly equal specific conductivities. He employed a vertical tube and observed the margin between a colored and a colourless solution. His results agreed very closely with those calculated from the conductivity measurements for the same concentration.

This method, however as stated above is very limited in its application on account of the difficulty of finding pairs of solutions that fulfill all the necessary conditions. It

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(1). Whetham. Phil. Trans. A. 337, (1893).

is also further limited by the necessity for the employment of a colored solution as indicator, since it is impossible to find an indicator with a suitably colored anion which will not give a precipitate, with such salts as those of the alkaline earth and the heavy metals.

The next work on this subject was done by Schrader (1). He undertook to investigate aqueous solutions containing mixtures of two electrolytes, such as potassium iodide and chloride, and in this manner determine the ratio between the ionic velocities of chlorine and iodine. He then compared these results with those obtained by Hittorf. He worked upon quite a number of salts, but his principal work was done with solutions of copper and cadmium salts. In his investigation he devised a form of apparatus that was different from that used by previous investigators, to overcome some of the defects to which they were subject. His apparatus was essentially a modification of that used by Kistiakowsky but cont in such a form that he could draw the liquid off from either electrode for analysis.

There still remained many serious defects in the forms of apparatus, in spite of the fact that many investigators had worked upon this problem.

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(1). Ztschr. elek. Chem. 5, 344.

All of these methods depend upon essentially the same principle, that is, the passage of a known amount of current through a solution of the electrolyte, and the subsequent separation and analysis of the solution around the electrodes, yet, the results obtained under similar conditions differ considerably. In the work of previous investigators they have either separated the solutions around the electrodes by porous diaphragms, or have relied upon the difference in specific gravity resulting from the electrolysis to secure a separation, and to secure this result have placed the anode and cathode at different levels in their apparatus.

Some of the most serious objections have been overcome in a form of apparatus devised in this University by Jones and Mather(1). The conditions which they wished to fulfill in the construction of this apparatus were as follows.

First, that it should be symmetrical in form in order that the current could be passed in either direction.

Second, that it should be large enough to contain a sufficient quantity of liquid to allow a large change in concentration.

Third, that it should be provided with a means of separating the two solutions around the electrodes after the electrolysis.

Fourth, that diffusion should be overcome as far as possible.

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(1). Amer. Chem. Journ. 26, 473, ([illegible]).

The apparatus which they devised to fulfill these conditions may be described as follows. It consists of two limbs united near the upper end by a U-tube, the bottom of which does not quite come to the lower ends of the limbs. At the center of this U-tube is a stop-cock of large bore. The lower ends of the limbs are closed with ground-glass stoppers, through which holes are bored and the electrodes inserted. The upper ends of the limbs above the U-tube are contracted to a comparatively small bore and graduated in millimeters in order to level the solution. This apparatus is then connected to a brass frame which, by means of a tube and clamp screw, can be secured in an upright position to a rod on the table or in the bath. This is then calibrated in order to determine the ratio between the contents of each side.

With this apparatus they could completely separate the solution arund one electrode from that around the other and accurately determine the increase in concentration on one side, and the decrease in concentration on the other.

The current in their investigation was measured by means of a silver voltameter.

They had, however, some difficulty in securing an accurate adjustment of level after the electrolysis in the first form of apparatus and therefore modified it somewhat.

The form of apparatus employed in these first determinations was a modification of that finally adopted, which is described above. In the form used at this time the limbs were of full size throughout the entire length with the stoppers at the top. The electrodes were at the end of glass tubes which were inserted through the stoppers and extended to the bottom of the limbs; and in order to secure adjustment of the level of the liquid in the two limbs it was necessary, at the close of the experiment, to slightly raise the stopper in order to permit the entrance of the air. This no doubt did not secure a very accurate adjustment of level in the two limbs, and this discrepancy was recognized by the investigators who then devised the final form as stated above.

This investigation, as will be seen from above, dealt chiefly with the improvement of the apparatus, the experiments being limited to solutions of silver nitrate in water and ethyl alcohol, and silver acetate in water.

In the investigation of these salts in the different solvents results were obtained which compared well with each other, although some difficulty was encountered in the investigation of silver acetate in aqueous solutions when the solutions were very concentrated, which was probably due to the forma-

tion of complex ions. They also tried the effect of allowing the electrolysis to proceed for different intervals of time, and from their results no difference could be detected in the relative velocities of the ions.

In their investigation of silver nitrate in ethyl alcohol, they came to pracitcally the same conclusions of Lenz (1), who was the only investigator that had worked upon alcoholic solutions of salts up to this time. His work was done some fifteen years before.

From their results they calculated the absolute velocities of the ions according to the law laid down by Kohlrausch, as far as data were available for the conductivity at infinite dilution of the solutions employed.

At the end of this investigation the following conclusions were drawn.

1. That the wide differences observed between the velocities of cation and anion at 0°C becomes less as the temperature rises; the velocities tending to become equal, as had been observed by others.

2. That the effect of decrease in concentration is in the same direction as that of increase in temperature.

3. That the velocities are largely dependent upon the nature of the solvent.

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(1). Mem. Petersb. Ak. 30, Nr, 9, (1882).

Since this investigation quite a number of papers have appeared upon this problem.

Gordon (1) since the time of Schrader's work has investigated the variations of temperature on cadmium salts in aqueous solutions. He states that the electromotive force of the element $Cd \,;\, Cd\,SO_4\,aq \,\vdots\, Cu\,SO_4\,aq \,\vdots\, \overset{+}{Cu}$ increase with temperature, indicating a diminution in the concentrations of the cadmium ions, which may be due to the formation of molecular aggregates. This was proved in the case of the halogen cadmium salts. On this assumption, the transference ratio should not be greater at higher than at low temperatures, i. e. the ratios of the weights of cadmium which has actually passed from the anode liquid to the quantity deposited on the cathode, or dissolved from the anode.

Hopfgarten (2) did some work similar to that of Schrader mentioned above, but it does not have any direct bearing upon the subject under investigation in this paper.

Kummel (3), however, has shown that the limiting values for

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(2). Ztschr. phys. Chem. 25, 115, (1898).
(1). Ztschr. phys. Chem. 23, 469, (1897).
(3). Wied. Ann. 64, 655, (1898).

migration constants of zinc and cadmium salts can be directly determined with the haloid compounds when the dilution is 1/100 to 1/500 normal, and that these values are also in keeping with the Kohlrausch law. In his investigation it appeared that the sulphates have complex ions and, therefore, do not give results consistent with the Kohlrausch law for the dilutions stated above. His method, however, is similar to that of Lodge.

The most elaborate investigation on this problem since the time of Hittorf was carried out by Bein (1). He describes in all five forms of apparatus with various means of separating the cathode solution from the anode solution. In one or two of these forms he makes use of a pinch cock to separate them. In another form he used the method devised by Loeb and Nernst; while in still another form he separates the liquids by means of a mercury column. It can be said that most of the forms of apparatus devised by Bein are very complex, probably more complex than is necessary.

The work of previous observers is also discussed at considerable length with special reference to the influence of diffusion on the values obtained.

The method used by the author consists in the analysis

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(1). Ztschr. phys. Chem. 27, 1, (1898); 28, 439, (1899).

of the anodic, mean, and cathodic liquids, various forms of apparatus being employed, according to the dilution of the electrolyte and the temperature required. All these are described and numerous figures are given. For sodium and hydrogen chlorides, the values were found to be almost independent of the concentration but vary with the temperature.

The transference numbers for anions are given by the expressions HCl $n_t = 0.157 + 0.0009\ t$;

NaCl $n_t = 0.622 + 0.00074\ t$.

For potassium chloride the values are

$n_{11} = 0.503$ and

$n_{76} = 0.513$

They were obtained and appeared to be independent of concentrations at least between the limit of one-fifth and one-hundredth normal.

For lithium chloride the values $n_{20} = 0.624$ and $n_{97} = 0.621$ were obtained in one-hundredth normal solutions, while $n_{25} = 0.672$ and $n_{97} = 0.610$ for one-fifth to one-twentieth normal solutions. For ammonium, rubidium, ceasium and thallium chlorides the values 0.507, 0.515, 0.598 and 0.516 were respectively obtained at about 20°. Calcium chloride gave results similar to those obtained for lithium chloride the

transference ratio changing but slightly with dilution at high temperatures.

For barium chloride n_{10} = 0.559 and n_{97} = 0.515 in solutions containing 0.04% chlorine.

For cadmium chloride n_{22} = 0.568 and n_{97} = 0.475 in solutions with 0.2% chlorine but at higher concentration the temperature change was much less.

Silver acetate gave the values n_{24} = 0.413 and n_{96} = 0.434, which, however, do not agree with the results of Nernst and Hittorf. Sulphuric acid gave numbers in accord with the expression $n_t = 0.160 + 0.0015\,t$ and these also differ from Hittorf's values.

For copper sulphate the values vary slightly with concentration and temperature and apparently gave a good maximum of 0.632 at 15°.

Silver nitrate gave the value n_{26} = 0.517 changing but slightly with temperature. The remaining determinations were made at temperatures of about 20° - 25° with the following results.

Salt	n		n
Strontium chloride	0.560	Thallium sulphate	0.528
Magnesium "	0.615	Magnesium "	0.541
Manganese "	0.613	Sodium carbonate	0.600
Cupric "	0.593	Potassium "	0.435
Cobalt "	0.581	Sodium hydroxide	0.799

Salt	n		n
Sodium bromide	0.[illegible]	Ammonium hydroxide	0.[illegible]
Potassium iodide	0,[illegible]	Calcium "	0.7[illegible]
Nitric acid	0.17[illegible]	Potassium permanganate	0.5[illegible]
Sodium nitrate	0.[illegible]	Succinic acid	0.[illegible]
Oxalic acid	0.21[illegible]		

Some determinations were also made by him in the case of solutions of concentrations from three to four times normal. The values obtained differ very considerably, however, from those at low concentrations and exhibit a much more marked temperature change. He also reviews the various values for transference ratios of salts obtained by different methods and is led to the general conclusion that the relative velocity of the Cation is in all cases less when a dividing membrane is used than when no such division is employed. This difference is most marked for animal membranes, and is small or negligible for porous clay divisions or parchment paper. In order to test the correctness of this conclusion, the transference ratios of hydrogen, sodium, lithium, calcium and cadmium chlorides were determined with various septa of (1) clay (2) parchment paper (3) fish bladder or (4) gold beaters skin, and in all cases the velocity of the Cation is diminished by uses of the last two membranes. The values obtained by Hittorf and others with membraneous septa are collectively [illegible]

compared with those obtained by the author. This influence of the membrane does not appear to depend on its general permeability, and the probable cause is briefly discussed. It may be due to a chemical activity of the membrane, which would hence possess the character of an acid or to polarisation induced by the current in the membrane. In either case the result is that membranes actually behave as partial semipermeable divisions.

The next work to be considered on this problem is that of O. Masson (1) who has devised a new form of apparatus for measuring absolute velocities. He recognized the doubtful validity of Lodge's method and the narrow scope of Whetham's and thus was led to devise a new method of measuring directly the velocity of ions. Two flasks each provided with a lateral opening are connected by a graduated, horizontal tube containing a mixed solution of gelatin and the salt to be investigated (compare Masson and Steele, Trans. 1899, 75, 725). The flasks contain suitable solutions into which the electrodes dip. These anode and cathode solutions must both be distinctly colored; the colored ion being the cation in the anode solution, and the anion in the cathode solution.

Further, the colored ions must migrate at a specifically

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(1). Ztschr. phys. Chem. 29, 501, 1899 ; Phil. Trans. 192 A, 331.

slower rate than the corresponding ions of the salt in the tube. A suitable anode solution is copper sulphate with a copper anode. A suitable cathode solution is sodium chromate with a platinum cathode.

When a current passes, the progress of the cations (for example K^+) in the colorless gelatin solution is accompanied by an equal advance of the blue Cu^+ ions; the anions (for example $C\ell$) are similarly followed by the yellow Cr O ions. The contents of the tube thus become blue at one end, colorless in the middle, and yellow at the other end. The relative length of the blue and yellow parts gives the ratio of the velocities of cation K^+ and anion $C\ell^-$. From this ratio the migration numbers can be calculated and compared with the values found by Hittorf.

The method depends essentially on the supposition that the progress of the colored ions is determined by the velocity of the colorless ions in front. Analysis showed that the bounding plane between colored and colorless zones is very sharp. The relative length of the blue and yellow parts remains constant throughout one experiment and is the same for different experiments at the same concentration. The ratio of the ionic velocities for the same salt is the same when potassium ferro-

chloride or potassium tartrate is substituted for sodium chromate. Theory, too, excludes any mixture of the ions, provided that the colored are specifically slower than the colorless ions which preceed them.

The migration numbers for the anion obtained from the ratio of the ionic velocities are, in the case of sodium, potassium, and ammonium salts, smaller than those found by Hittorf, whose values, however, hold for more dilute solutions than those used by the author.

Contrary to Hittorf's observation, the migration number for the $\overset{-}{C}l$ ion seems to decrease slightly with increasing concentration.

The relative velocities of the ions are compared with Kohlrausch's numbers, and a fair agreement is found. The absolute velocities are smaller than in aqueous solution.

Kohlrausch (1), about this same time published an investigation upon the velocity of ions in dilute aqueous solutions up to one-tenth normal working in all cases at 18° C. He showed that for solutions of one-twentieth to one-tenth of the normal concentration the conductivities of compounds composed of univalent ions or of univalent ions in union with bivalent ions, may be calculated from the ionic velocities, which, in this case, depend for each univalent ion on concen-

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(1). Ann. phys. Chem. (N F), 66, 785, (1898).

tration only. This does not hold for compounds composed of bivalent ions only. For these compounds the velocities vary in each case with increasing concentration, in the same regular manner from the velocities in solutions of infinite dilution, so that if l is the velocity in a solution of concentration n, and l_∞ the velocity at infinite dilution $l = l_\infty - Q n^{1/3}$ where Q is the constant for all ions. If the conductivity is given in cm^{-1} ohm^{-1}, and the concentrations in gram equivalents per litre, Q has the value 213. This, however, does not hold for the hydroxyl ions of the bases or the hydrogen ions of the acids, as the decrease in velocity with rising concentration is far more marked in these cases. The fall in the velocities of the bivalent ions is also not quite the same when these ions are in union with univalent ions, as when in union with other bivalent ions.

All ions in solutions of infinite dilution have velocities entirely independent of the other ions with which they are associated.

Among the later investigations on the subject is that of Steele (1). The method employed by him is in principle the same as that of Masson in that the velocity of movement of a layer between two solutions is measured, the measured ion being

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(1). Journ. Chem. Soc. 79, 414, (1901).

followed in all cases by an indicator ion of specifically slower velocity. Like the method of Masson it is also a method of comparison. In a given experiment the velocities of the boundaries at the anode and cathode end of a homogeneous solution are compared, both being driven by the same, unknown, potential fall per centimeter. The method differs, however, from Masson's in two essential respects; first, the measurements are made in water and not in gelatin, and second, the employment of a colored ion as indicator is not necessary. All that is required is that a solution of the indicator containing about the same number of gram-molecules per litre as the measured salt solution should differ from the latter in density and refractive power. The choice of indicators is thus very largely increased. Still this method fails to determine accurately A U and A V, since it has not as yet been found possible to measure U directly, although this may be calculated very approximately.

The essential feature of this method consists in the imprisonment of the aqueous solution to be measured between two partitions of gelatin containing the indicator ion in solutions, thus preventing displacement of the liquid during the course of the experiment.

The results obtained from his experiments confirm those

previously calculated.

The only apparatus which differs to any considerable extent from that used by previous experimenters has been devised by A. A. Noyes(1). It consists of U-tubes attached by rubber tubing, the electrodes being inserted into the long arm of the tubes, and these filled with a solution to only a few centimeters above the bend. After electrolysis he divided the solution into three separate portions. With this apparatus Noyes has done some very accurate work. He made use of this apparatus especially in the determination of the relative velocities of the ions of such salts as potassium chloride, sodium chloride, etc. In these experiments he used platinum electrodes, and titrated the alkali and acid as they were formed around the electrodes by means of burettes inserted into the stoppers.

So far no work has been done in dilute solutions and it was important that this point especially should be investigated. The next work on this problem was done by Jahn(2) and a number of students working under him in the University of Berlin. They used an apparatus differing from any previously employed but resembling in some points that used by Noyes.

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(1). Ztschr. phys. Chem. 36, 61, (1901).
(2). Ztschr. phys. Chem. 37, 673, (1901).

Their apparatus consisted of a vessel of the form of an Erlenmeyer flask connected with a U-tube which made connection with a larger part of the apparatus which could be varied in size according to the dilution of the solution to be used. The anode which was inserted into the part of the apparatus which could be changed and consisted of the metal, silver copper, cadmium and etc., according to the salt under investigation or dissolved in the acid formed; while the cathode consisted of mercury which made connection with the circuit by means of a copper wire protected by a glass or rubber tube, the mercury being covered by a copper sulphate solution. By means of this apparatus they determined the transference numbers of the following acids and salts; hydrochloric and nitric acids, sodium, lithium, barium and cadmium chlorides, potassium, sodium and cadmium bromides, silver nitrate, cadmium iodide, cadmium and copper sulphate.

In the determination with hydrochloric acid an amalgamated zinc rod was used as the anode, while in the case of nitric acid the anode consisted of a silver rod which had previously been amalgamated.

In the determination of the migration velocities with the alkali and alkaline earth salts, the amalgamated zinc rod was used. In every case they made an analysis, both of the anode solution and the neutral layer.

In their investigations on silver nitrate, the cadmium salts, and copper sulphate, they used the metal carefully purified for the anode and in the x determinations were able to determine the difference in concentration by making an analysis for the metal itself. In this investigation they also determined the effect of dilution upon the relative velocities, and found that in many cases, such as in the cadmium salts, they did not become constant until dilution between 200 and 500 were reached. They compared their results with those obtained by Bein and Hittorf and they agreed very well with the exception of lithium chloride, which agreed much better with the results obtained by Kuschel.

From all the work done up to this time there still is a limit in the dilution at which it becomes impossible to measure the transport numbers. Even in the work of Jahn and his pupils, Noyes and Bein the dilutions are limited. In Jahn's work he could not get very accurate results above a dilution of one hundred and fiftieth normal, and this range is not sufficient to measure the constant transport numbers of many salts, especially the diad and triad salts of which only a few have previously been determined. Steele and Denison(1) undertook to measure the transport numbers of salts at dilutions

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(1). Journ. Chem. Soc. 81, 456, (1902).

comparable with those at which accurate conductivity measurements are made and also to test whether at such dilutions the transport numbers would become constant. They selected the salts of calcium for their experiments because good measurements of their conductivities had been made at dilutions of $n = 0.0001$. Thus to work at dilutions comparable with the conductivity measurements they would have to work with solutions varying between one two hundred and fiftieth normal to one four hundredth normal, it not being practicable to work at much greater dilutions on account of the impossibility of purifying such large quantities of water which would be required for the experiments. In such dilute solutions as these referred to above they showed that it was obvious that, in order to get an appreciable quantity of the salt carried by the current, a large volume of solution would have to be electrolysed or, by using small volumes, the experiment would have to be carried for a long time to get an appreciable change in concentration. Of the two alternatives the former was chosen because in using the latter method the experiment would be in danger of being lost on account of a backward diffusion caused by the differences in concentration in the middle layer. However, by selecting the former alternative and employing the usual method, the apparatus would be of unmanageable size.

With these facts in view they devised an apparatus which admits of the electrolysis of almost unlimited volumes of liquids.

The apparatus used by them consisted of a W-shaped tube which was connected with a reservoir to which fresh quantities of solution could be added as that in the apparatus was drawn off at the bottom of the limbs in the W-shaped tubes. The acid and alkali formed were neutralized by the addition of small quantity of N/2 alkali and acid respectively. The addition of this also overcame the concentration changes which would necessarily be formed and cause diffusion back into the tube. By using an apparatus constructed in this manner they could draw off each side separately, and then refill the apparatus from the reservoir, and allow electrolysis to proceed, until several litres of solution had been passed through the apparatus. In their investigation they determined the transport numbers for cupric chloride, copper sulphate, cupric nitrate, as well as for potassium chloride. The current was measured by a silver voltameter.

The values which they found for potassium chloride agree satisfactorily with all the best values obtained by other investigators in this field, and also confirm Kohlrausch's assumption as to the constancy of the transport number for

salts of this class with increasing dilution.

Steele[1], after the investigation carried out by himself and Denison proceeded with the investigation, using the apparatus formally used by himself and described above in this paper. In this investigation the transport numbers of such salts as barium chloride and magnesium sulphate were determined. He came to the following conclusions concerning the results obtained.

(1). The transport number is not independent of the concentration. This had already been pointed out by others.

(2). The specific ionic velocity of the cation varies with the particular salt under investigation.

(3). The current measured by the galvanometer is not the same as that calculated from the observed velocities.

The explanation that the specific ionic velocities vary with the concentration, and vary more for some ions than for others, he attributed to the formation of complex ions in solution, but this means a motion of at least a portion of the undissociated salt along with the ions, and consequently the concentration of the solution at the margin is altered, and this interferes with the regularity of the potential fall;

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(1). Phil. Trans. 198, A, (1901).

the velocity of the margin being correspondingly affected. With these points unsettled, Abegg and Gauss(1) undertook to investigate these points raised by Steele. They investigated the influence of the initial concentrations of the neighboring electrolytes and recommended that in Steele's method the concentration of the indicator jelly should be at least equivalent to that in the middle electrolyte.

They attributed the differences between the results obtained by Hittorf's method and those obtained by the direct method of Steele to the influence of cataphoresis on the moving boundaries and showed that when a correction for this influence is applied, the transport number for chloride is the same as that found by Hittorf.

The effect of electrical endosmose, having been shown in only one case, Denison(2), now studying at the University of Breslau, undertook to investigate a number of salts, and measure accurately this endosmose, and, if possible, ascertain its effect on the transport numbers.

The method used by him was practically that used by Steele. A few changes were made in the apparatus by which he could measure the endosmose and also obtain a constant voltage.

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(1). Ztschr. phys. Chem. 40, 737, (1902).
(2). Ztschr. phys. Chem., 44, 575, (1903).

He showed very clearly that in salts of the alkali metals with the exception of lithium, if proper allowance be made for the endosmose, very accurate results can be obtained. He found the same exception with lithium chloride as had been found by previous investigators, for instance, it exhibits an increase in the transport number for the anion with increase in concentration.

Upon investigating salts which were capable of forming complex ions or undergoing hydrolysis, the values obtained for the transport numbers did not agree with those obtained by Hittorf, even after this correction had been applied, but there is a parallelism between the two series of results.

In a water solution where the electrolytes were separated by gelatin, he also observed that crevices occurred in the gelatin which began by the appearance of a bubble of gas, and that this rapidly grew and became a large space.

This, as was referred to above, was a serious difficulty which Lodge and Masson had encountered. But he succeeded in showing that this did not change the potential fall in the middle electrolyte but did make small differences in the endosmose, which had to be taken into account.

In this investigation he also studied the effect of gelatin on the transport numbers. He observed that the transport

numbers measured in gelatin solution are the same as those obtained in aqueous solution, so long as the gelatin is liquid, the concentration of the gelatin exerts no influence.

In solidified gelatin the transport numbers are quite different, and it appears that under these conditions the velocity of the cation is retarded relatively to that of the anion; the absolute velocity in gelatin being slower than in water. Thus, the transport number for the anion in gelatin always appeared too large. A similar phenomenon is observed in very concentrated aqueous solutions, and it is very probable that in both cases the specific frictional coefficient of the ions, as well as the formation of complex ions, play an important part.

He also considers it probable that the gelatin enters into combinationwith certain salts forming complex cations. He also states, in support of this view, that it may be pointed out that various proteids have the power of combining with acids and alkalies forming compounds of a salt-like character, and therefore there are good reasons for regarding the proteids as weak acids and bases. They, themselves, have practically no ionizing tendency, but the salts which they form with strong acids and bases have a strong ionizing power.

It is thus very probable that gelatin or some product formed by hydrolysis would act in this way, and would, as suggested, be a solution of an acid or base in gelatin, would contain no free acid or base until an excess was added. This would explain the above difference in the transport numbers in liquid and solid gelatin.

Very little work has been done in any other solvent than water. A few determinations were made ten or twelve years ago by Lenz and some by Mather in his dissertation at this University, but still the field is practically unworked.

Carrara (1) undertook an investigation in this field quite recently and has determined the transport numbers in methyl alcohol solutions for different dilutions of the following salts; silver, copper, cadmium, lithium nitrates, silver, copper, cadmium and lithium chlorates, copper and cadmium chlorides, cadmium, lithium, tetra, ethyl ammonium and trimethyl ammonium iodides, copper sulphate, cadmium and copper acetates.

He used three different forms of measuring apparatus. One was an apparatus with a membrane similar to one of the forms used by Hittorf. Another was that used by Loeb and Nernst, while the third he describes as a new form of apparatus. This

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(1). Gazz. Chim. Ital. 33 I, 241, (1903.)

third form is in fact a slight modification of that used by Mather in this University, but he does not even mention the work carried out by Mather, nor does he even give him any credit for devising this form of apparatus.

In his investigation he comes to some general conclusions which have been brought out before by a number of investigators, for instance, he states that the transport numbers vary considerably with the concentration, the values sometimes indicating the existence of complex ions in solution, especially with such salta as cadmium iodide. He, however, brings out an interesting point in the investigation of lithium chloride. In this case his results indicate the existence of complex ions even in a binary electrolyte. This he assumes can only be explained by considering lithium chloride in solution to have the formula Li_2Cl_2 and that when this dissociates it may dissociate into the ions $LiCl_2$ and Li. The power of forming these complex ions was found to vary considerably for different salts.

On comparing the transport numbers found by him for the same salt in aqueous and methyl alcohol solutions, it is seen that the difference between them is in general very small, and of the same order of magnitude as the differences obtained by a change of concentration. In general the transport numbers

for the salts in methyl alcohol are higher than in water solution; only three exceptions have been found. These were the following salts; lithium chlorate, cadmium chloride and cadmium iodide.

From these considerations he draws the conclusion that the transport numbers of the ions of an electrolyte tend toward the same value independent of the solvent in which it is dissolved. In other words, if the dilution is sufficiently great and no secondary reactions take place, the transport numbers of an electrolyte are the same in all solvents.

The transport numbers found for solutions of salts in methyl alcohol are the same as in aqueous solutions at greater concentrations.

The most recent investigations upon this subject were made by Huybrechts (1) and Wolff (2). Nothing new, however, is brought out by their work on this subject. They used an apparatus which was a very slight modification of that used by Jahn and his pupils. Huybrechts' investigation was to determine the transport numbers for sulphuric acid and magnesium sulphate in very dilute solutions.

Wolff's investigation had to do with barium chloride and hydrochloric acid.

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(1). Dissertation, University of Berlin. (1902).
(2). " " " " (1903).

As has been already stated, in most of the investigations, however, aqueous solutions have been dealt with and comparatively little work has been done in solvents other than water. The only work that was done in any solvent other than water was that of Lenz, Mather, and the recent work of Carrara.

EXPERIMENTAL WORK.

This investigation was undertaken for the purpose of determining what effect mixtures of methyl alcohol and water would have on the relative velocities of the ions of such a salt as silver nitrate.

The work of Jones and Lindsay (1) on the conductivity of certain salts in water, methyl, ethyl and propyl alcohols and mixtures of these solvents suggested this work.

In his work Lindsay (1) found that the conductivity of such salts as potassium iodide, ammonium bromide, strontium iodide, etc. were less in mixtures of the solvents than in either of the solvents alone. Especially was this the case in mixtures of methyl alcohol and water.

Considering these facts the first thing to determine was

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(1). Amer. Chem. Journ. 28, 329, (1902).

whether silver nitrate would give similar conductivity results, and if so whether there was any relation between this phenomenon and the relative velocities.

The conductivities of silver nitrate in these solvents and varying mixtures of them were determined.

The water, methyl and ethyl alcohol were purified by the methods given by Lindsay.

In each case a mother solution was made in the particular solvent, and the remaining solutions were obtained by successive dilutions with some of the solvent of the same composition. In this an error was avoided which would result from the contraction, when alcohol and water were mixed, and also prevent the accompanying heat effect.

In some cases as in very dilute solutions where such small quantities of the mother solution were required, a second mother solution was made from the first, and the more dilute solutions made from it in the way described. The strength of these mother solutions was determined by titrating with a standard solution of ammonium sulphocyanate.

Conductivity Apparatus Employed.

The apparatus described and used was similar to that used by Lindsay. They differed from the ordinary Arrhenius cell, being provided with a ground glass top to prevent evaporation of the more volatile solvents, and also protect

the anhydrous alcoholic solutions from the moisture of the outside air. The glass tubes carrying the electrodes were slipped through thin rubber tubes in the cap. Sealing wax was then run over the outside of the joint.

The zero bath was prepared as follows. A large glass battery-jar was filled with finely crushed ice and distilled water. This was then placed in a water bath and the space between then filled with finely crushed ice and water. This proved very efficient as it was possible to keep within 0.05° of zero for hours. The bath at 25° was of the ordinary form and was kept in constant motion by a stirrer driven by means of a hot air engine.

The thermometers used could be accurately read to 0.02 of a degree.

The burettes and flasks were also carefully calibrated.

Conductivity Measurements.

All the conductivity measurements were made at the two temperatures 0° and 25°. In the following tables

v = number of litres of solution containing a gram molecular weight of the salt.

$\mu_v 0^\circ$ = molecular conductivity at 0°

$\mu_v 25^\circ$ = " " at 25°.

Table I. Molecular Conductivity of Silver Nitrate in Water.

v	$\mu_v 0^\circ$	$\mu_v 18^\circ$
10	[illegible]	[illegible]
20	[illegible]	[illegible]
40	[illegible]	[illegible]
80	63.16	115.81
160	65.38	119.80
320	69.91	125.05
640	71.05	125.90
1280	70.59	127.35

Table 2. Molecular Conductivity of Silver Nitrate in Ethyl Alcohol.

v	$\mu_v 0^\circ$	$\mu_v 18^\circ$
9.71	7.11	
19.43	8.90	[illegible]
38.86	11.35	[illegible]
77.73	13.10	20.11
155.47	15.13	23.87
310.95	17.04	26.16
621.89	[illegible]	30.62

Table 3. Molecular Conductivity of Silver Nitrate in Methyl Alcoh

v.	$\mu_v 0°$	$\mu_v 25°$
10	2[illegible].36	[illegible]
20	32.63	[illegible]
40	39.71	[illegible]
80	45.28	61.9[illegible]
160	51.09	70.36
320	56.71	[illegible]0.17
640	61.42	8[illegible].22

Table 4. Molecular Conductivity of Silver Nitrate in Ethyl Alcohol 25%, and Water.

v	$\mu_v 0°$	$\mu_v 25°$
38.86	25.35	[illegible].70
77.73	26.65	[illegible]
155.47	[illegible]	[illegible]
310.95	28.72	[illegible].27
621.39	[illegible]	[illegible]

Table 5. Molecular Conductivity of Silver Nitrate in Ethyl Alcohol 50% and Water.

v.	$\mu_v 0^\circ$	$\mu_v 25^\circ$
19.43	12.35	37.89
38.86	15.31	[illegible]
77.73	17.01	[illegible]
155.47	17.93	[illegible]
310.93	18.10	47.13
621.89	19.90	49.59
1243.78	20.79	[illegible]

Table 6. Molecular Conductivity of Silver Nitrate in Ethyl Alcohol 75% and Water.

v	$\mu_v 0^\circ$	$\mu_v 25^\circ$
19.43	13.12	27.01
38.86	14.30	30.43
77.73	16.79	[illegible]
155.47	[illegible]	35.34
310.93	[illegible]	38.01
621.89	[illegible]	40.14

Table 7. Molecular Conductivity of Silver Nitrate in Methyl Alcohol 25% and Water.

v	μ_v 0°	μ_v 25°
40	33.65	72.58
80	36.95	75.56
160	39.03	79.51
320	41.03	82.79
640	41.25	85.91

Table 8. Molecular Conductivity of Silver Nitrate in Methyl Alcohol 50% and Water.

v	μ_v 0°	μ_v 25°
20	27.37	53.35
40	29.[illegible]	56.80
80	29.93	59.75
160	31.57	63.32
320	33.39	65.35
640	34.67	66.07

Table 9. Molecular Conductivity of Silver Nitrate in Ethyl Alcohol 75% in Water.

v	μ_v 0°	μ_v 25°
20	27.96	48.30
40	30.05	52.53
80	32.51	57.17
160	35.22	61.31
320	38.71	63.25
640	40.27	69.42

Table 10. Temperature Coefficients of Conductivity of Silver Nitrate in Water (0° - 25°).

v	Temperature Coefficient.
10	1.75
20	1.56
40	1.[illegible]
80	2.10
160	2.14
320	2.21
640	2.20
1280	2.10

Table 11. Temperature Coefficient of Conductivity of Silver Nitrate in Ethyl Alcohol. (0° - 25°).

v	Temperature Coefficient.
19.43	0.214
38.86	0.224
77.73	0.300
155.47	0.380
310.95	0.377
621.89	0.468

Table 12. Temperature Coefficient of Conductivity of Silver Nitrate in Methyl Alcohol (0° - 25°).

v	Temperature Coefficient.
10	0.392
20	0.482
40	0.540
80	0.707
160	0.771
320	0.355
640	1.102

Table 13. Temperature Coefficients of Conductivity of Silver Nitrate in Mixtures of Ethyl Alcohol and Water of various compositions.

Temperature Coefficients.

v	25% alcohol	50% alcohol	75% alcohol
[illegible]		0.905	[illegible]
38.86	1.35	0.962	[illegible]
77.75	1.44	1.015	[illegible]
155.47	1.49	1.059	0.658
310.95	1.45	1.121	[illegible]
621.89	1.58	1.180	0.823
1243.78		1.280	

Table 14. Temperature Coefficients of Conductivity of Silver Nitrate in mixtures of Methyl Alcohol and Water of various compositions.

Temperature Coefficients.

v	25% alcohol	50% alcohol	75% alcohol
20		1.04	0.810
40	1.46	1.15	[illegible]
80	1.54	1.19	0.97[illegible]
160	[illegible]	1.27	[illegible]
320	[illegible]	[illegible]	1.100
640	1.71	[illegible]	[illegible]

In order to see the connection existing between the conductivities in each solvent the following tables are given for comparison.

Table 15. Comparison of the Molecular Conductivities of Silver Nitrate in Ethyl Alcohol and Mixtures of it with Water at 35° C.

v.	25% alcohol	50% alcohol	75% alcohol	100% alcohol
19.43		37.87	27.01	14.2[illegible]
38.36	59.70	39.50	30.[illegible]3	16.96
77.73	62.75	4[illegible]2	33.65	20.11
155.47	63.32	45.15	35.94	23.[illegible]
310.95	64.37	47.13	39.01	26.[illegible]
621.39	68.28	49.39	40.14	30.[illegible]

It is seen from these values that the molecular conductivity in ethyl alcohol and mixtures with water does not show a minimum in the ordinary range of dilution, but still does not obey the law of mixtures. This is in accordance with Lindsay's work on potassium iodide. In that case he did not find a trace of a minimum at 35°.

These values in table 15 are plotted as curves in Fig. I, the abscissae representing the different percents of alcohol and the ordinates the molecular conductivities.

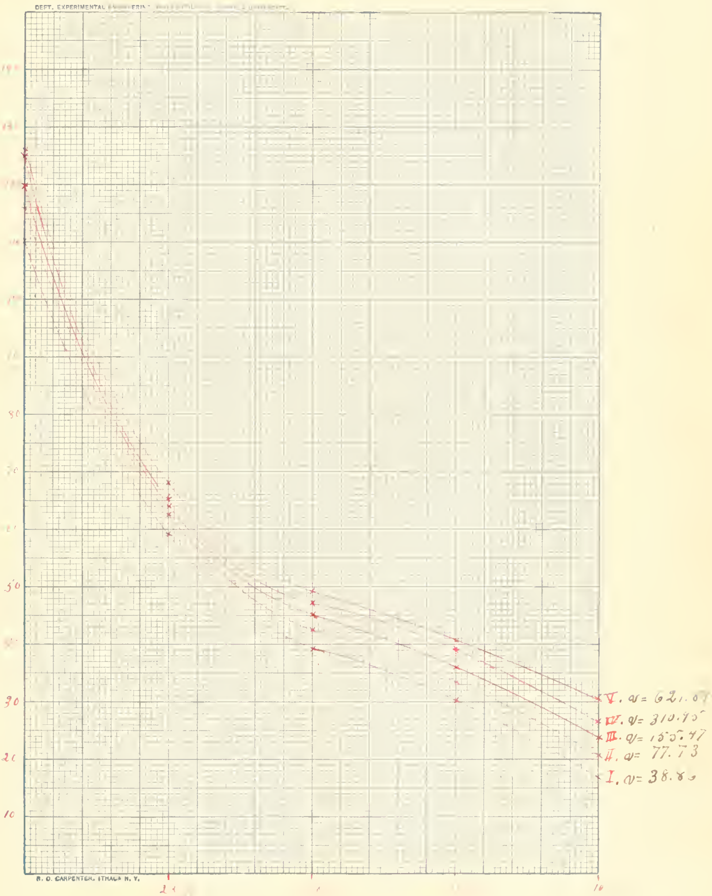
DEPT. EXPERIMENTAL ENGINEERING
80
70
50
30
20
10
V. v= 621.07
IV. v= 310.95
III. v= 155.47
II. v= 77.73
I. v= 38.85
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Table 16. Comparison of the Molecular Conductivities of Silver Nitrate in Ethyl Alcohol and Mixtures of it with Water at 0° C.

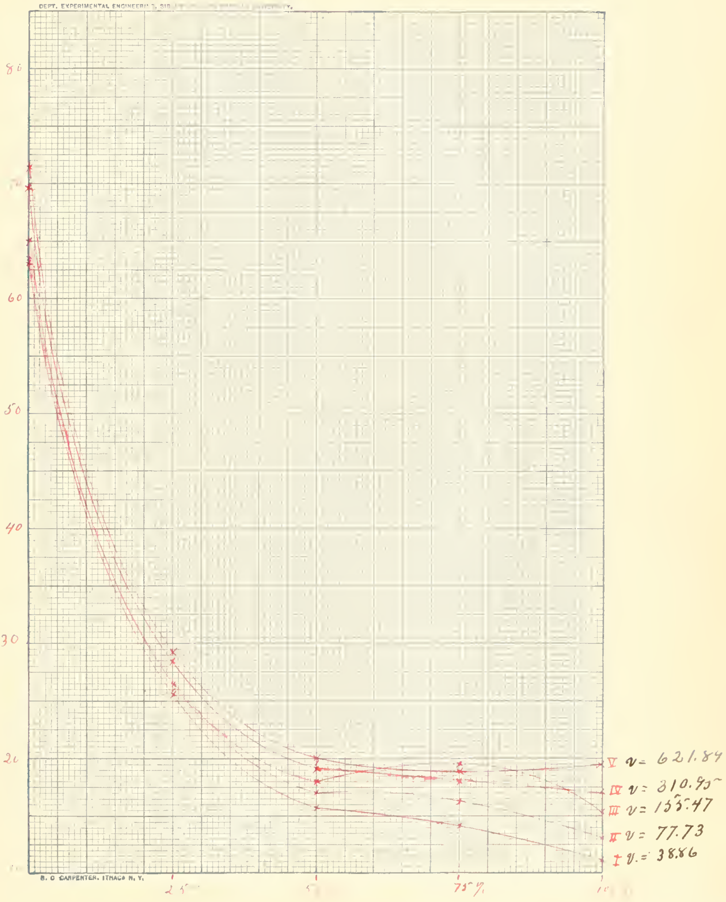
v.	25% alcohol	50% alcohol	75% alcohol	100% alcohol
9.71				7.11
19.43		15.25	13.12	9.00
38.86	25.95	15.81	14.30	11.[illegible]
77.73	26.65	17.04	16.79	13.10
155.47	26.45	17.92	19.48	15.15
310.95	27.72	19.10	18.00	17.01
621.89	28.84	19.30	19.41	19.43
1243.78		20.79		

These values are plotted in Fig. II. The curves are of the same general form as in Fig. I. No distinct minimum is shown, but the form of the curve indicates that a minimum value is approached.

Table 17. Comparison of the Molecular Conductivities of Silver Nitrate in Water, Methyl Alcohol and Mixtures of these Solvents at 25° C.

v.	water	25% alcohol	50% alc.	75% alc.	100% alcohol.
10	99.46				35.77
20	105.72		53.53	4[illegible].20	41.07
40	110.3[illegible]	72.[illegible]	56.[illegible]0	52.55	5[illegible].4[illegible]
80	115.[illegible]1	76.[illegible]6	59.[illegible]5	57.17	[illegible].05
160	119.86	79.5[illegible]	65.[illegible]	61.53	70.[illegible]
320	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
640	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1280	[illegible]				

Fig No II


DEPT. EXPERIMENTAL ENGINEERING, SIBLEY COLLEGE, CORNELL UNIVERSITY.
80
70
60
50
40
30
20
10
25
50
75 %
100
V v = 621.84
IV v = 310.95
III v = 155.47
II v = 77.73
I v = 38.86
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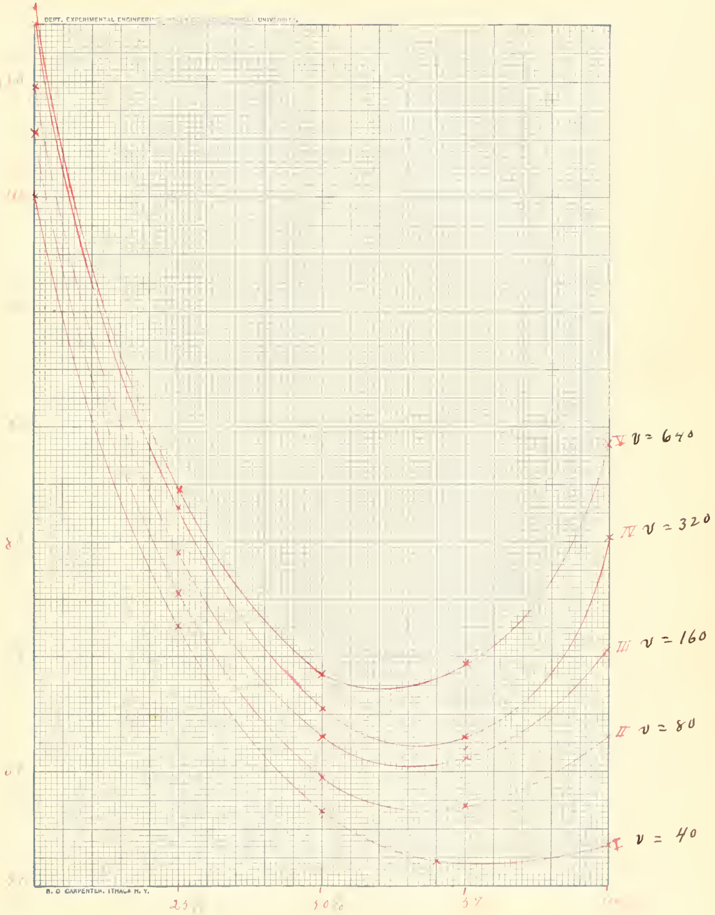
These values are plotted in Fig. III. In nearly every case the minimum as shown by the curve lies between mixtures of the solvents containing respectively 50% and 75% of alcohol.

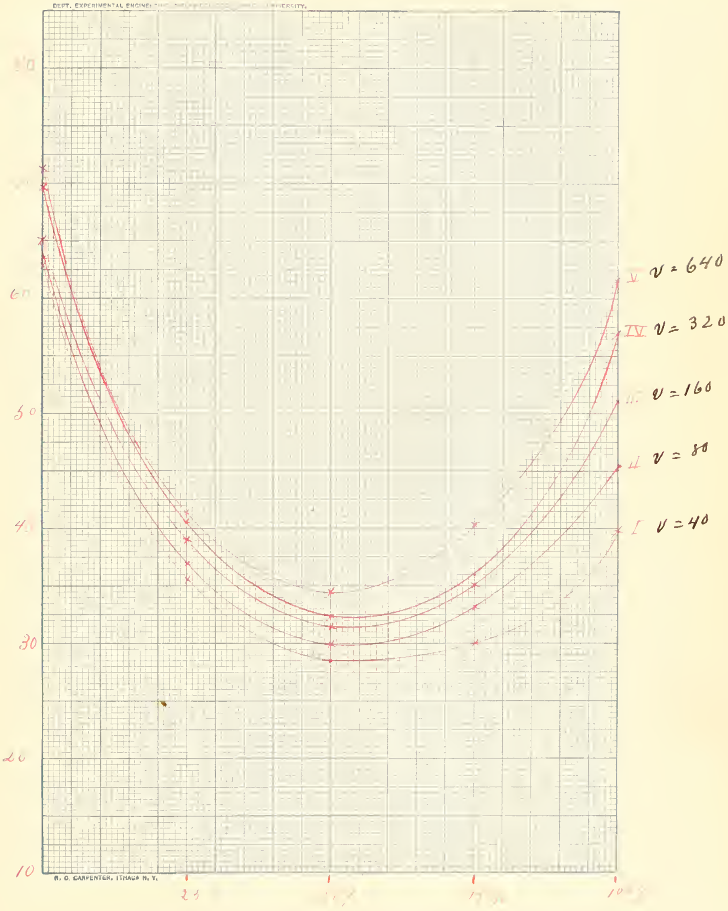
Table 18. Comparison of the Molecular Conductivities of Silver Nitrate in Water, Methyl Alcohol and mixtures of these solvents at 0° C.

v	water	25% alcohol	50% alc.	75% alc.	100% alcohol.
10	55.72				[illegible]
20	58.63		27.27	27.98	[illegible]
40	63.10	35.[illegible]3	28.63	30.05	[illegible]
80	65.16	36.95	29.93	32.81	45.[illegible]
160	65.38	39.03	31.47	33.22	51.09
320	69.91	41.03	33.29	35.71	56.71
640	71.05	41.25	34.67	40.27	61.[illegible]
1280	70.59				

These results are plotted in Fig. IV. The curves are of the same general form, as the curves in Fig. III. They differ, however, in a few points. The chief difference is that the minimum point has shifted to the left corresponding now to an alcohol-water mixture not far from 50%.

Fig. No. 14


DEPT. EXPERIMENTAL ENGINEERING, CORNELL UNIVERSITY.
V v = 640
IV v = 320
III v = 160
II v = 80
I v = 40
8
6
B. C. CARPENTER, ITHACA N. Y.
25 %
50 %
75


DEPT. EXPERIMENTAL ENGINE… UNIVERSITY.
80
70
60
50
40
30
20
10
25
10
V v = 640
IV v = 320
III v = 160
II v = 80
I v = 40
R. O. CARPENTER, ITHACA N. Y.

From the above results it is clear that silver nitrate is not an exception to the general relation [illegible].

It was now interesting to see what effect alcohol would have upon the relative velocities of the ions, especially in the mixtures of methyl alcohol and water. This case seemed to offer a good field for investigation. Therefore, this particular part of the problem was taken up for investigation, although a few determinations of relative velocities were made in ethyl alcohol.

Relative Velocities of Ions.

In the last few years a large number of investigations have appeared on the relative velocities of ions. Most of them, however, have had to deal with aqueous solutions of a large number of substances. Few, however, have determined the relative velocities in methyl and ethyl alcohol, and nothing has been done upon mixtures of these solvents.

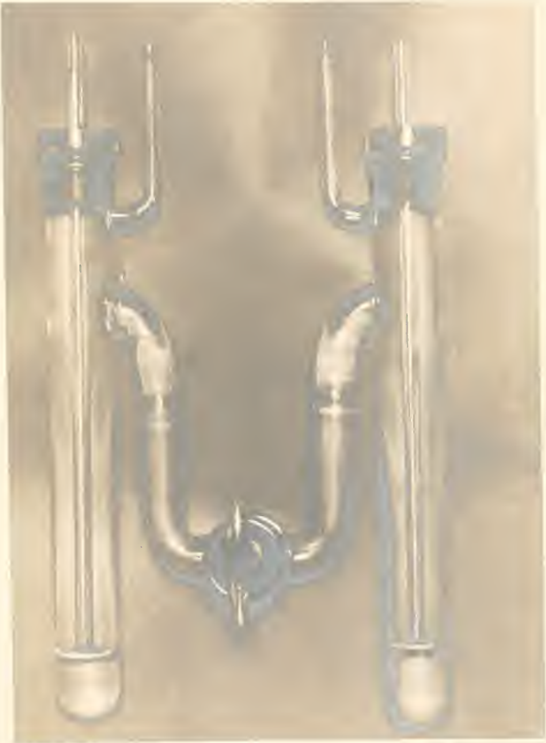
In most of the later investigations new forms of apparatus have been devised, many of them being very complicated. The question arises whether such a high degree of complexity is necessary for effecting the electrolysis and separation of the solutions. In many of the new forms no special means were provided for the final separation of the solutions, some depending simply upon the difference in specific gravities of

the solutions resulting from the electrolysis. Discrepancies in the results are, therefore, probably due in part to the incomplete separation of the two portions of the solution. But one form has been devised which prevents diffusion. This apparatus was devised by Jones and Mather in this University and has been fully described above.

From an examination of the different forms of apparatus that used by Mather seemed best adapted for this investigation, but some very serious difficulties pointed out in part by Mather in his paper had to be overcome. These difficulties, however, were avoided by devising the apparatus shown in Plate I.

The two limbs are 20 cm. long and 2 cm. in diameter, with the electrodes inserted from the top through ground glass stoppers. Just below the stoppers two small tubes are attached, which extend outward and upward, the vertical part being graduated in millimeters. The lower part of this small tube is 5 millimeters in diameter, and the vertical part is about 3 millimeters.

The limbs are connected, 3 cm. below the stoppers, by a U-tube 1 1/2 cm. in diameter, in the same plane with the limbs. The bottom of the U-tube is 5 cm. above the lower ends of the limbs. At the center of the U-tube is a stop cock of 5 mm.



bore.

The electrodes were made of pure, round silver plates, into which a platinum wire was riveted in order to seal them into glass tubes running through the ground-glass stoppers. The small amount of platinum exposed in the bottom of the silver plate was covered by a thin coating of fusion glass.

The glass tubes were then firmly secured in the ground-glass stoppers by means of a piece of black rubber tubing which wasplaced on the tube and through which the tube was forced. The electrical connection was then made by filling the tubes with mercury, which made connection with the silver plate by means of the platinum wire riveted into the plate, as was stated above.

This form of apparatus could easily be placed in a thermostat on hooks arranged for thatpurpose which supported the apparatus under the U-tube.

In order to keep a constant temperature the thermostat bath represented in Plate II was constructed. This proved to be very efficient remaining constant to within 0.1°, and at the same time affording plenty of room for three pieces of apparatus and voltameters. It consists of a wooden box 2 ft. long, 14 inches wide and 10 inches deep, lined inside with heavy galvanized iron. The iron lining extends to within

one-half an inch of the top of the wooden box.

One and one-half inches from the top of the box a heavy movable shelf was arranged in which the three voltameters could be placed and kept at a constant temperature. In the bottom of the wooden box a hole 14 inches square was lined only with metal so that a small flame could be applied. Hooks were then arranged on the side of the bath opposite the shelf for the voltameters, and for the apparatus represented in Plate I, which was suspended from them. The box was then filled with water to the level of the shelf, and kept at constant temperature by means of an Ostwald thermo-regulator.

In order to secure a uniform temperature the water in the bath was kept in constant motion by a stirrer, which was driven by a small hot-air engine.

For determinations at 0° C the bath was filled with finely broken ice, and the apparatus placed in the bath in the same manner as in the 25° bath. The wooden casing of the bath, in determinations at this temperature, serves as a poor conductor of heat.

All of the electrical connections attached to the bath were placed upon a block of hard rubber to prevent any loss of current.

Special precautions were also taken in all the wiring about the bath. Flexible insulated wire was used in the wiring, and wherever two wires crossed additional precaution was taken to run them through rubber tubing. The box was also heavily shellaced as an additional precaution.

Two currents of different strengths were used. One current of 60 volts was supplied by a storage battery. The other current of 110 volts was supplied directly from the power house. In every case the current was measured by means of a voltameter, consisting of platinum crucibles and pure silver anodes. The platinum crucibles were placed in weighing flasks to insulate them entirely from each other, and, at the same time, to serve as a convenient means of placing them upon their supports in the constant-temperature bath.

Connections with the circuit were made by placing the platinum crucible upon a copper plate, to which a wire had been soldered.

The anode of pure silver was suspended in the platinum crucible, by running it through a rubber stopper, which fit the weighing glass and also served as a cover to it. The silver anode was also inserted into a clean linen bag to prevent any small particles, which become detached from the anode, from falling into the crucible and therefore being weighed with the silver deposited by the current.

The platinum crucibles were treated with fused acid potassium sulphate, then boiled with nitric acid, heated in the flame of the blast lamp, cooled in a desiccator and weighed before each experiment. The deposit formed by the current was treated in accordance with the directions recommended by Richards (1) in his investigation upon the determination of the chemical equivalent of copper and silver.

Preparation of Solutions.

The analysis in every case was made by titration with ammonium sulphocyanate, ferric ammonium sulphate being used as the indicator. Special care was taken in the preparation of the solutions, and their strength was determined by titration with standard solutions of potassium chloride.

In the preparation of the solutions of potassium chloride the pure salt which had been purified especially for conductivity work, was used. Small amounts of this salt were weighed and dissolved in water. It was then titrated against the silver nitrate.

The silver nitrate used was Kahlbaum's best material which was free from any detectable impurities.

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(1). Ztschr. phys. Chem. 41, 302, (1902).

The water used in the preparation of the solutions was obtained by redistillation of ordinary distilled water essentially by the method described by Jones and Mackay(1). The ordinary distilled water, to which a solution of chromic acid had been added, was boiled and the steam passed through a boiling solution of barium hydroxide.

The absolute alcohol was prepared by distillation from quick lime, further dehydrated with anhydrous copper sulphate, and finally distilled from a small amount of sodium just before using. In the preparation of the solutions in absolute alcohol the following method was adopted. The silver nitrate was placed in a dry measuring flask. The latter was filled with alcohol by means of a siphon from the bottle containing the alcohol which had been distilled from sodium. The alcohol was thus not allowed to come in contact with moisture. The bottle was closed by a two-hole rubber stopper. Through one hole the siphon passed and through the other the drying tube which permitted the air to enter the flask. The siphon led to a Gooch funnel which was also closed with a two-hole rubber stopper. The siphon passed through one hole and another drying tube through the other hole. This funnel was then connected with the measuring flask and alcohol siphoned into it.

The resulting solution of silver nitrate was then removed to a dry bottle which was closed with a rubber stopper,

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(1). Amer. Chem. Jour. 1[illegible], [illegible], (1[illegible]).

connection with the interior being made by a glass tube and rubber tube.

When it was desired to draw off part of the solution either for analysis or to fill the apparatus, the point of a burette was connected with the glass tube in the bottle, by means of a rubber tube, and then the solution was drawn up into the burette by aspiration through a drying tube which closed its upper end. The burette was then connected with one of the small graduated tubes on the apparatus the other one being closed by a Bunsen valve. The two small tubes were then connected and the apparatus tilted first one way and then the other in order to remove the last trace of air from beneath the stoppers. Each tube was then closed with a Bunsen valve, and the apparatus placed in the constant temperature bath. The connections with the circuit and voltameter being made the electrolysis was begun.

Calibration of Apparatus.

The first calibration of the apparatus was by weighing first the empty apparatus, then, with one side full of water, and then with both sides full. In this way the exact contents of the apparatus could not be determined but the ratio between the two sides could be obtained.

The second and subsequent calibrations were made by measuring the contents of each side with a burette, which

had previously been calibrated by means of the apparatus designed by Morse and Blalock (1).

Calibration No. I. December 7, 1903.

Apparatus No. I.

Weight of empty apparatus	[illegible]
" " apparatus with left side full of water	356.3[illegible]
" " " full of water	[illegible]
Therefore left side contains	50.377½
right " "	[illegible]

Apparatus No. II.

Weight of empty apparatus	[illegible].52
" " apparatus with left side full of water	330.91
" " " full of water	396.50
Right side contains	49.32[illegible]
Left "	50.07[illegible]

Apparatus No. III

Weight of empty apparatus	2[illegible]7.79
" " apparatus with left side full of water	[illegible]
" " " full of water	[illegible]
Right side contains	[illegible]9.45[illegible]
Left "	[illegible]

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(1). Amer. Chem. Journ. 16, 479, (1894).

Calibration No. II. January 11, [illegible].

Apparatus No. I.

Contents of right side	[illegible]7.71 cc
" " left "	[illegible] cc
Right Side contains	[illegible] %
Left Side "	50.38 %

Apparatus No. II.

Contents of right side	[illegible].37 cc.
" " left "	[illegible] "
Right Side contains	[illegible].07%
Left " "	[illegible]

Apparatus No. III.

Contents of right side	[illegible] cc
" " left "	[illegible].74 "
Right Side contains	[illegible]
Left " " .	50.515[illegible]

Calibration No. III. February 1[illegible], 190[illegible].

Apparatus No. I.

Contents of right side	[illegible] cc
" " left side	[illegible].11 "
Right side contains	[illegible]
Left " "	[illegible]

The position of electrodes in this apparatus were changed just before the calibration.

Apparatus No. II.

Contents of right side	[illegible] cc.
" " left side	[illegible]2 cc.
Right side contains	50.11[illegible]
Left " "	[illegible]9.[illegible]36[illegible]

Apparatus No. III.

Contents of right side	[illegible].50 cc
" " left "	[illegible] "
Right side contains	[illegible]9.[illegible]8 %
Left " "	50.552%

Calibration No. IV. March [illegible], [illegible].

Apparatus No. I.

Contents of right side	68.35 cc.
" " left side	6[illegible].[illegible] "
Right side contains	49.963%
Left " "	50.037%

Apparatus No. II.

Contents of right side	66.10 cc.
" " left side	6[illegible].5[illegible]
Right side contains	49.447%
Left " "	50.533%

Apparatus No. III.

Contents of right side	6[illegible].[illegible]5 cc.
" " left side	6[illegible].55 "
Right side contains	49.447%
Left " "	50.553%

Measurement of Relative Velocities.

Knowing the relation between the two sides of the apparatus, the experiments were carried out as follows. The apparatus was filled from the burette as described above, to the zero mark on each side. The open ends of the small leveling tubes were then closed by Bunsen valves and the whole placed in the bath by supporting it on hooks arranged for that purpose. The water in the bath and the solution in the apparatus were practically the same height, as the apparatus was immersed until the bottom of the ground-glass stoppers were on a level with the surface of the water.

Connection with the circuit and voltameters being made, the electrolysis was allowed to proceed until enough silver was deposited in the voltameters to be weighed accurately, the deposit usually weighing between 0.05 to 0.10 of a gram. The time of the electrolysis depended upon the resistance offered by the solution.

At the close of the electrolysis the apparatus was removed from the bath and the level of the solution in the apparatus brought to corresponding graduations on each leveling tube. The stopcock was then closed. The contents were then carefully washed, filtered through glass wool or washed asbestos

to remove any disintegrated silver, made up to a known volume and analyzed. The accuracy of the results was determined by comparing the amount of silver found on analysis with that calculated from the amount of solution placed in the apparatus at the beginning of the experiment.

With this data the relative velocity of the ions could easily be calculated as follows.

The amount of silver found in the apparatus as a whole was multiplied by the percent contained on the side that increased, thus giving the amount of silver contained on that side at the beginning of the experiment.

This was then subtracted from the amount found on that side by analysis, which gave the amount of increase due to electrolysis. This increase was then divided by the weight of the silver deposited in the voltameter, the result being the relative velocity of the anion.

The strength of the current in no case exceeded 0.005 amperes.

Silver Nitrate in Water.

In these determinations the apparatus was filled and the experiment carried out as described above.

After the electrolysis each side was carefully washed out, filtered through glass wool and diluted to 200 cc.

Aliquot parts of this were then taken and titrated against a standard solution of ammonium sulphocyanate.

At the beginning of this investigation the titrations of several of the determinations were made with N/10 ammonium sulphocyanate, but it was soon found that this was too concentrated to give good results, as the burette could not be read with sufficient accuracy to obviate a large experimental error. Another very serious difficulty was that, in titrating such a strong solution against a comparatively weak one in many instances, the smallest fraction of a drop that could be used would go considerably beyond the neutral point.

To prevent these experimental errors the titrations were made with a N/25 ammonium sulphocyanate solution. With a solution of this strength the point of change could easily be distinguished, and the erroe in reading the burette would be diminished since a larger volume of solution would be used.

The results of these determinations are given in the following table.

In this table as in all subsequent tables the following symbols will be used.

t = temperature of the bath where used.

m = concentration of the solution in gram-molecular weights per litre.

x = change in concentration expressed in number of cc of N/10 silver nitrate.

v = amount of silver in grams, deposited in the voltameter.

a = velocity of the anion.

Table 19. Relative Velocities of the Anion of Silver Nitrate in Water at 25°.

t	m	c	v	a
25°	0.1	20.964	0.4320	0.5238
25°	0.1	20.054	0.4126	0.5260
25°	0.1	12.705	0.2622	0.5230
25°	0.1	12.432	[illegible]	0.5307
25°	0.1	13.006	0.2517	0.5287

Values obtained by other observers, although at different temperatures, are given in the following table.

Table 20. Relative Velocity of the Anion of Silver Nitrate determined by other Observers in aqueous solution at different temperatures.

t	m	a	
29°.1	0.1	0.5317	Mather
45°	0.025	[illegible]	"
47°.5	0.1	0.5250	"
47°.9	0.1	0.5272	"
47°.4	0.1	0.5286	"
19°	0.148	[illegible]	Hittorf
19°	0.035	0.526	"
19°	0.024	0.526	"
20°	0.1023	[illegible]	Nernst & Loeb
30°	0.0511	[illegible]	"
36°	0.0256	[illegible]	"
80°	0.0703	[illegible]	"

Table 21. Relative velocity of the Anion of Silver Nitrate in Aqueous Solution at 0^{0} C.

m	c	v	[illegible]
0.102	6.3370	0.1214	[illegible]
0.102	6.4940	0.1229	[illegible]
0.102	6.2480	0.1198	[illegible]

Table 22. Relative Velocity of the Anion of Silver Nitrate as determined by other Observers in Aqueous Solution at 0^{o}.

m		
0.1	0.5414	Mather
0.1	0.5401	"
0.1	0.5413	"
0.025	0.5377	"
0.025	0.5380	Nernst & Loeb.

These values differ considerably from those obtained in this investigation at the same temperature.

In the determination of the first three by Mather, he measured the current with an d'Arsonval galvanometer and by this means only determined the average strength of the current, this probably introduced a considerable experimental error.

In the two last determinations in table 22 the current in both cases was measured by a silver voltameter, but the con-

centration of the solution was less, and, as is well known, a decrease in concentration diminishes the relative velocity of the swifter ion.

Table 23. Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at 25° C.

m	c	v	a
0.1012	2.593	0.0510	0.6122
0.0765	[illegible]	0.1021	0.5903
0.0763	[illegible]	0.1015	[illegible]
0.0784	5.345	0.0942	0.6121
0.094	3.025	0.0665	0.5905
0.094	4.017	0.0840	0.5932

The solutions of Silver Nitrate in ethyl alcohol offered great resistance to the current and where the large changes in concentration were obtained the current was allowed to run for ten or twelve hours.

Table 24. Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 25°.

m	c	v	a
0.100	8.964	0.1655	0.5849
0.100	8.971	0.1684	[illegible]
0.100	[illegible]	0.1517	[illegible]
0.093	[illegible]	[illegible]	[illegible]
0.093	[illegible]	[illegible]	[illegible]

A much larger change in concentration was obtained in these determinations than in those in ethyl alcohol, because the silver nitrate was considerably more soluble in methyl than in ethyl alcohol, and thus the electrolysis could proceed further without danger of the determination being lost on account of the cathode and anode liquids becoming mixed.

Table 25. Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 0°.

m	c	v	a
0.097	5.4570	0.0659	0.5[illegible]65
0.097	5.8530	0.0722	0.5[illegible]98
0.096	5.1447	0.0572	0.5533
0.096	2.[illegible]750	0.0[illegible]52	0.5561
0.096	5.096[illegible]	0.0572	0.5642

Table 26. Relative Velocity of the Anion of Silver Nitrate in a Mixture of 25% Methyl Alcohol and Water at 25°.

m	c	v	a
0.I	6.6240	0.1285	0.5[illegible]
0.1	6.4550	0.1[illegible]58	0.55[illegible]
0.1	6.28[illegible]0	0.1[illegible]51	0.551[illegible]

Table 27. Relative Velocity of the Anion of Silver Nitrate in a Mixture of [illegible]% Methyl Alcohol and Water at 0°.

m	c	v	a
0.103	3.7[illegible]	0.0748	0.5428
0.103	3.668	0.0741	0.5366
0.104	4.01[illegible]	0.0[illegible]1	0.5517
0.10[illegible]	4.089	0.082[illegible]	0.55[illegible]
0.104	4.25[illegible]	0.0851	0.559[illegible]
0.10[illegible]	4.374	0.085[illegible]	0.5[illegible]02
0.104	4.51[illegible]	0.0851	0.5474
0.103	3.197	0.0[illegible]5[illegible]	0.[illegible]27[illegible]

Table 28. Relative Velocity of the Anion of Silver Nitrate in a Mixture of 50% Methyl Alcohol and Water at [illegible]°.

m	c	v	a
0.104	[illegible].17[illegible]	0.1104	0.603[illegible]
0.104	[illegible].310	0.113[illegible]	0.603[illegible]
0.104	5.147	0.111[illegible]	0.5965

Table 29. Relative Velocity of the Anion of Silver Nitrate in a Mixture of 50% Methyl Alcohol and Water at 0°.

m	c	v	a
0.1048	2. 080	0.5720	0.5[illegible]
0.10[illegible]8	3.1540	0.[illegible]10	0.530[illegible]
0.1048	3.11[illegible]0	0.65[illegible]0	0.[illegible]501

Table 30. Relative Velocity of the Anion of Silver Nitrate in a Mixture of 75% Methyl Alcohol and Water at 25°.

m	c	v	a
0.104	[illegible]	0.1006	[illegible]
0.104	[illegible]	[illegible]	[illegible]
[illegible]	4.474	[illegible]	[illegible]
0.107	1.903	0.0348	[illegible]
0.107	[illegible]	[illegible]	[illegible]

Table 31. Relative Velocity of the Anion of Silver Nitrate in a Mixture of 75% Methyl Alcohol and Water at 0°.

m	c	v	a
0.099	[illegible]	[illegible]	[illegible]
[illegible]	3.021	0.0578	[illegible]
0.099	3.055	0.0580	[illegible]
0.096	[illegible]	0.0571	[illegible]
0.098	3.035	[illegible]	[illegible]
0.095	[illegible]	0.0319	[illegible]

In order to see the connection existing between the relative velocities of the anion of Silver Nitrate in Water, Methyl alcohol and the various mixtures of these solvents, the following table is given.

Table [illegible]. Relative Velocity of the Anion of Silver Nitrate in Water, Methyl Alcohol and Mixtures of these Solvents.

t	0	25	50%	75%	100%
25°	0.5285	0.5538	0.6010	0.5902	0.5797
0°	0.53[illegible]	0.5379	0.5391	0.5673	0.5[illegible]71

The values in this table are plotted in Fig. V; the abscissae representing the percent of alcohol and the ordinates representing the relative velocity.

The curve at 25° shows a maximum value in the 50% mixture, while at 0° a minimum value is shown in the same solvents. The curves are also exactly opposite in every respect.

The course of the curves may be explained as follows. The law of Kohlrausch (1) shows that the molecular conductivity at infinite dilution is equal to the sum of two independent constants which are in fact the velocities of the ions at infinite dilution calculated in terms of conductivity units, that it, $A + C = \mu_\infty$ - A representing the anion and C the cation, and μ_∞ conductivity at infinite dilution.

In this investigation, however, the conductivity at infinite dilution in these various solvents has not been determined, but by Ostwald's (2) modification of the law of Kohlrausch, which takes into account the amount of dissociation, which is represented as follows $\alpha (A + C) = \mu_\infty \alpha$ represent-

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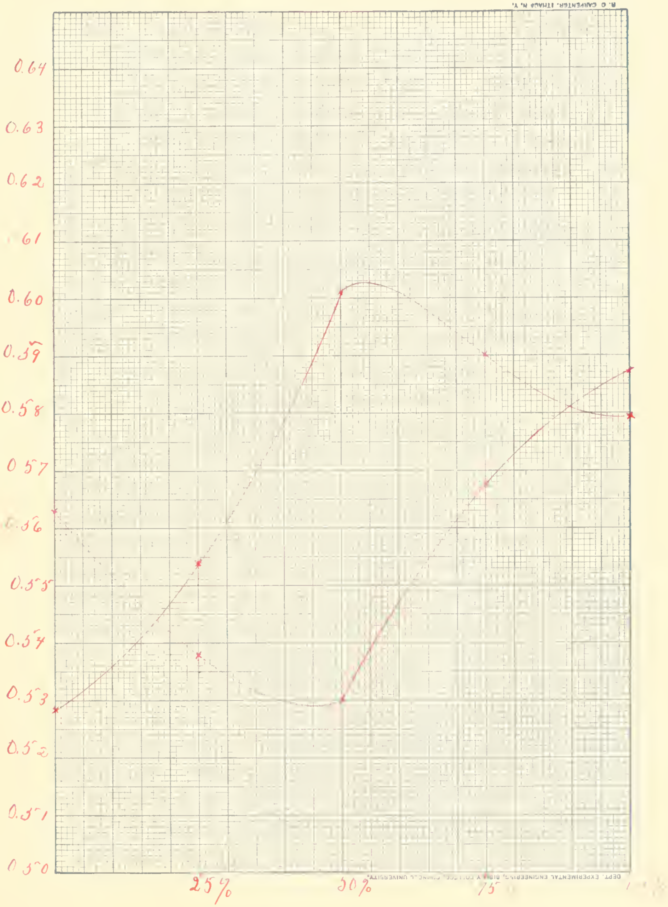
(1). Wied Ann. 26, 194, (18[illegible]).
(2). Lehrb. d. allg. Chem. II, [illegible].

Fig V


0.64
0.63
0.62
0.61
0.60
0.59
0.58
0.57
0.56
0.55
0.54
0.53
0.52
0.51
0.50
25%
50%
75
100%
A. O. CARPENTER, ITHACA N.Y.
DEPT. EXPERIMENTAL ENGINEERING, SIBLEY COLLEGE, CORNELL UNIVERSITY

ing the percent dissociation, it is possible to calculate α A and α C at any dilution if the ratio C/A is known. The ratio C/A has been determined for tenth normal solution of Silver Nitrate in these various solvents.

Hence, if we have the conductivities at 0° and at 25° of any dilution we may calculate λ C and α A, assuming that C/A is the same for dilutions of about the same degree, which is not improbable. This has been done in the following table for a dilution of v = 40.

Table 34. Velocities of the Anion and Cation of Silver Nitrate in Water, Methyl Alcohol and Mixtures of these solvents calculated in conductivity units.

	CH_3OH 0%	CH_3OH 25%	CH_3OH 50%	CH_3OH 75%	CH_3OH 100%
Anion 25°	58.25α	40.24α_1	34.65α_2	30.88α_3	30.96α_4
" 0°	35.51α	19.18α_1	15.71α_2	17.05α_3	23.31α_4
Cation 25°	51.97α	32.44α_1	22.15α_2	21.45α_3	22.46α_4
Cation 0°	27.59α	16.46α_1	12.93α_2	12.99α_3	16.40α_4

Having calculated these values of α C and α A for the two temperatures 0° and 25° we may calculate the temperature coefficients of ionic mobility, not the true coefficients, however,

but γ_1 (a constant) times the true coefficient. The variation of γ, as was shown by Jones & Douglas(1) is not appreciable over a range of twenty five degrees and, therefore, the above procedure is allowable. This has been done in the following table.

A_{25} represents the ionic velocity of the anion at 25° measured in conductivity units.

A_0 represents the ionic velocity of the anion at 0° measured in conductivity units.

ΔA represents the difference in the velocities of the anion, between 0° and 25° or is equal to $A_{25} - A_0$.

C_{25} represents the ionic velocity of the cation at 25° measured in conductivity units.

C_0 represents the ionic velocity of the cation at 0° measured in conductivity units.

ΔC represents the difference in the velocities of the cation between 0° and 25° or is equal to $C_{25} - C_0$.

Φ_{25} represents fluidity of the solvent at 25°.

$\Delta \Phi_0$ represents the difference in the fluidity between 0° and 25° or is equal to $\Phi_{25} - \Phi_0$.

Δt represents difference in temperature or 25° - 0°.

Φ_0 represents fluidity of solvent at 0°.

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(1). Amer. Chem. Journ. 26, 428,(1901).

Table 35. Comparison of the Relative Temperature Coefficients of Ionic Mobility for the Ions of Silver Nitrate in Water, Methyl Alcohol and various Mixtures of these Solvents, also the Temperature Coefficient of Mobility of Solvent.

	CH_3OH 0%	CH_3OH 25%	CH_3OH 50%	CH_3OH 75%	CH_3OH 100%
$\frac{1}{A_{25}}\cdot\frac{\Delta A}{\Delta t}$	0.0156α	$0.0209\alpha_1$	$0.0230\alpha_2$	$0.0179\alpha_3$	$0.0098\alpha_4$
$\frac{1}{C_{25}}\cdot\frac{\Delta C}{\Delta t}$	0.0189α	$0.0197\alpha_1$	$0.0166\alpha_2$	$0.0153\alpha_3$	$0.0106\alpha_4$
$\frac{1}{\phi_{25}}\cdot\frac{\Delta \phi}{\Delta t}$	0.0249	0.0233	0.0216	0.0205	0.0121

The temperature coefficients of mobility of the solvents were calculated from the results of Traube(1), Pagliani(2) and Batelli(3).

The relative temperature coefficients for the anion and cation in the same solvent are strictly comparable, since α is a constant and therefore does not affect the result of the comparison.

From a consideration of this data it is seen that in the pure solvents, water and methyl alcohol, the coefficient for

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(1). Ber. 19, 871, (1889).
(2). Att. d. R. Ac. delle. Sc. d. Torrino. 207, (1885).
(3). " " " " " " "

the cation is greatest whereas in the mixture that of the anion is greater. This being the case, C/A in the pure solvents would approach the limiting value 0.5, as the temperature rises, and the beginning and end of the curve of relative velocities at 25° would be below the beginning and end the curve for 0°.

Since in the mixtures the anion has a greater temperature coefficient, the curve for 25° will pass through a maximum; this maximum existing in that mixture where the irregularity between the two temperature coefficients is greatest, that is, the 50% mixture.

If we know the value of α - the dissociation factor, we could calculate the true temperature coefficients from the relative coefficients.

At the dilution used ($v = 40$) the dissociation of silver nitrate in water is about 89%, or $\alpha = 0.89$. It has been shown by Carroll (1) in the case of certain salts, sodium iodide, potassium iodide and potassium bromide, that in 50% methyl alcohol $\alpha = 0.91$ for $v = 32$, and 0.93 for $v = 64$. We should not make an appreciable error if we assume the value 0.91 for α in the case of silver nitrate in the 50% mixture at $v = 40$. The real temperature coefficient would then be

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(1). Dissertation Johns Hopkins University. 1904.

0.0230 x 0.91 = 0.0212. Kohlrausch(1) has pointed out in the case of certain ions in aqueous solutions that the more nearly the temperature coefficients of ionic mobility and fluidity (of water) are equal, the greater is the effect of decrease in fluidity in lowering ionic mobility. This would probably be true for ions in mixed solvents.

Comparing, then, the temperature coefficients of mobility of anion the cation, and fluidity of the 50% mixture, it is seen that the temperature coefficient of the $\overline{NO}_3$ ion (0.0212) is most nearly equal to that of fluidity (0.0218). Hence the effect of decrease in fluidity would be greatest in the case of the NO_3 ion; that is, C/A would approach the limiting value 0.5, and, hence the minimum in the curve in the 50% mixture.

The fluidity is also decreased by change of composition and the resulting change in ionic mobility will be greatest in the case of that ion whose temperature coefficient is most nearly equal to the temperature coefficient of fluidity. This is the case with the NO_3 ion, therefore this ion will be the most greatly effected, and the ratio between its velocity and that of the $\overset{+}{Ag}$ ion will become less; that is approach the limit 0.5, and there will therefore be a minimum in the curve.

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(1) Sitz. Ber. d. Berlin Ak., 572, (1902).

CONCLUSIONS.

1. A study of the conductivity of silver nitrate in water, methyl alcohol and mixtures of these solvents, leads to the conclusion that, silver nitrate is not an exception to the general phenomenon discovered by Zelinsky and Krapiwin (1) and studied extensively by Lindsay in this University. The minimum point in the conductivity was found for silver nitrate in these solvents at 25° as well as at 0°.

2. The conductivity of silver nitrate in water, ethyl alcohol, and mixtures of these solvents does not show a minimum point either at 25° or at 0°, but a study of the curves representing these conductivities leads to the conclusion that, at 0° a minimum is approached.

3. By comparing the conductivities at 0° with those at 25°, the conclusion can be drawn that the influence of one solvent on the other decreases with rise in temperature.

4. The differences in the relative velocities observed in the pure solvents at 0° and 25° become less as the temperature rises, and the velocities, therefore, tend toward equality. This has already been observed for pure solvents, but it does not hold in the case of mixed solvents. That exactly the

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(1). Ztschr. phys. Chem. 21, 35, (1897).

opposite is true in most instances is seen by examining Fig. V.

5. The relative velocities are largely dependent on the nature of the solvent.

6. In mixed solvents the relative velocities are dependent on both the temperature and composition of the mixture.

Biographical Sketch.

The author of this paper, Harry Preston Bassett, was born on September 7, 1878 near Cynthiana, Harrison Co., Kentucky.

He received his preparatory instruction at Smith's Classical School, Cynthiana, Kentucky. He entered the State College of Kentucky in the Fall of 1898, and graduated in June 1901, receiving the degree of Bachelor of Science.

During the year 1901 he was instructor in Chemistry in the State College of Kentucky, and at the same time pursued studies leading to the degree of Master of Science, which he received in June 1902. In the Fall of 1902 he entered the Johns Hopkins University as a graduate student in Chemistry, with Chemistry, Physical Chemistry, and Physics as his subjects of study.

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